

SYNTHESIS, CHARACTERIZATION AND ELECTRICAL PROPERTIES OF BRIDGED TETRAPYRAZINOPORPHRAZINE NICKEL (II)

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ABSTRACT

A bridged complex structure of Tetrapyrazinoporphanazine, $PzNi(II)$ with 1,4-dicyanobenzene(DCN) was prepared. The study shows that the complex has the structure $(PzNi(DCN))_n$ with $n=1$ or more. It is analyzed by elemental analysis and spectroscopic methods (IR, electronic and 1H NMR), in addition to the thermo- gravimetric and X-ray diffraction methods. The dc electrical conductivity measurements show that the bridged complex has a semiconducting behavior with activation energy of 1.12 eV compared with the activation energy of $PzNi$ which is 0.74 eV. The study shows two possible structures, triangular bipyramidal square planner or octahedral.

KEYWORDS: Bridged, Tetrapyrazinoporphanazine, Dc Electrical, Conductivity

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INTRODUCTION

Tetrapyrazinoporphanazines (PzM) (where Pz and M are tetrapyrazine, and metal respectively) are semiphthalocyanine compounds which have two nitrogen atoms at the equivalent 1,4 positions of the phthalocyanine benzene rings⁽¹⁾. Pz is less electron rich than the corresponding phthalocyanine(Pc) due the presence of the nitrogen atoms⁽²⁾. Both Pc and Pz have remarkable thermal and chemical stability and have many interesting optical properties(absorption and emission) and have many applications such as organic solar cells, chemical sensors and photodynamic therapy(PDT) as photosensitiser for cancer treatment ,^(3,4). The spectroscopic and electrical properties are affected by the type of central metal atoms and peripheral substitutions on the rings⁽²⁾. Bridging of phthalocyanines and tetrapyrazinoporphanazines with different bridging ligand groups such as Fluorine atoms, bibyridine and CN is well known, which affect solubility, aggregation, optical and electrical properties⁽⁵⁻¹¹⁾. In this work we prepared a complex of tetrapyrazinoporphanazine Nickel (II) which is bridged with 1,4-dicyanobenzene. The complex then identified by spectroscopic thermal and X-ray diffraction in addition to a study of the effect of bridging on the electrical properties. A suggested structure is shown in figure 3.

PREPARATION OF THE COMPOUNDS

Preparation of Dicyanopyrazine, DCP⁽¹²⁾

A mixture of 1 ml (2.18mmol) of Glyoxal, 25 ml ethanol and 25 drops of acetic acid was added to a conical flask containing 2.36g (2.18 mmol) of diamino-malonitrile (DAMN) soluble in 25 ml of ethanol. The reaction mixture then refluxed for four hours and then left for two days to be precipitated. The solid product was filtered and recrystallized from 1:1 mixture of acetone/ hexanol. The product is pale yellow crystalline material mp (222-225 °C), (yield is 1.6g, 56.1%). CHN, calculated ($C_6H_2N_4$): C: 55.33, H: 1.53, N: 43.24 Found C: 54.48, H: 1.26, N: 42.24. The preparation reaction is shown in figure 1.

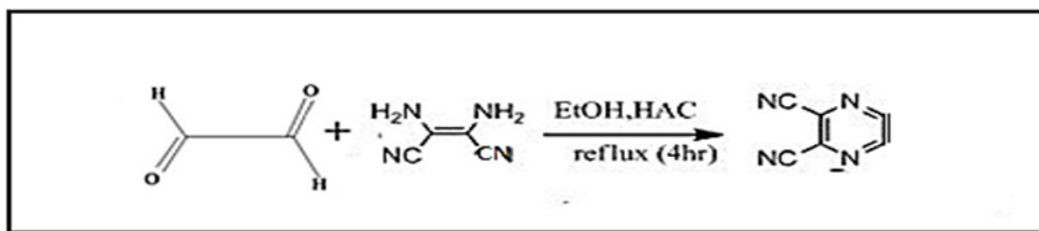


Figure 1: Preparation of DCP

Preparation of Tetrapyrazinoporphrazine Iron (II), PzFe

0.52 g (4mmol) of DCP was dissolved in 100 ml flask containing of 0.237g (1mmole) of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.24g (4 mmol) of Urea. The mixture refluxed with magnetic stirring for two hours and then cooled to room temperature and filtered⁽¹³⁾. The solid product then purified by dissolving it in 2 ml of chloroform and added drop wise with stirring to 100 ml of ethanol. The purification process was repeated for three times and the solid product was dried at 100°C .

The product is pale bronze powder, mp (254-257). The yield is 0.41g (71.81%). CHN, calculated ($\text{C}_{24}\text{H}_8\text{N}_{16}$): C: 50.01, H: 1.40, N: 38.90; Found C: 49.35, H: 1.35, N: 35.40. The preparation reaction is shown in figure 2.

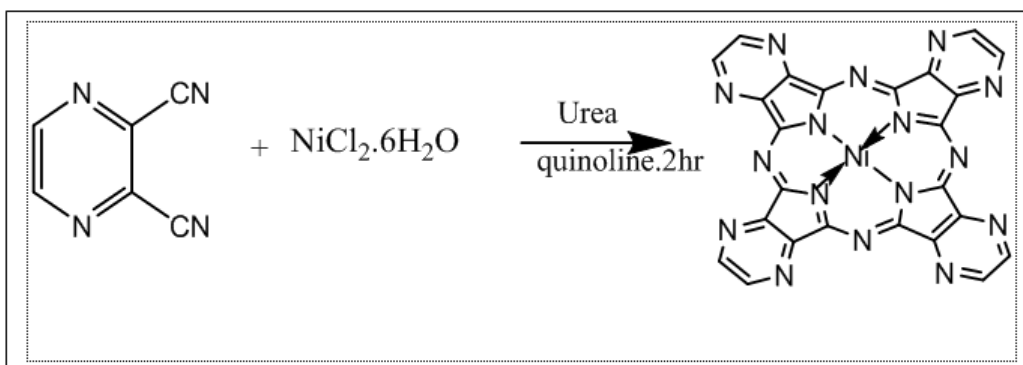
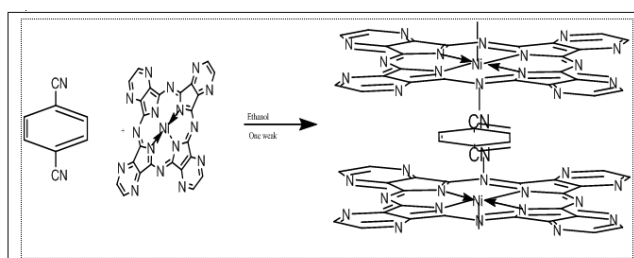


Figure 2: Preparation of PzNi Complex

Preparation of Tetrapyrazinoporphrazine Iron (II) Bridged with p- dicyano benzene ($\text{PzNi}(\text{DCB})_n$)

0.128g(1mmol) of 1,4- dicyanobenzene was added to a round bottomed flask containing 0.579g of PzNi(1mmol) dissolved in 10 ml of ethanol. The mixture then refluxed for a week and cooled. The solid product then purified by dissolving it in 2 ml of THF and added portion wise with stirring to a beaker containing 100 ml of hexane. The precipitate then filtered and dried at 100°C . The product is dark bronze powder. The yield is 0.45g (63.55%). CHN, calculated ($\text{C}_{56}\text{H}_{20}\text{N}_{34}\text{Fe}_2$) C: 52.25, H: 1.55, N: 37.07; Found C: 51.18, H: 1.31, N: 35.23. The reaction is shown in figure 3.

Figure 3: Preparation of $\text{PzNi}(\text{DCB})_n$

Identifications of the Compounds

The little differences between the calculated and experimental values are mainly due to the big size of the molecules and the difficulty of the purification.

Spectroscopic Identification

IR: Figure 4, shows the IR spectrum of the complex PzFe. It shows the distinctive aromatic C-H stretching vibration at 3193 cm^{-1} and aromatic C-H bending in plane 1037 cm^{-1} and out of plane at 769 cm^{-1} . The band at 1635 cm^{-1} stretching vibration for C=N. The stretching vibration at 1498 cm^{-1} is related to the aromatic C=C. The stretching of the C=N bands for both pyrole and pyrazine are mixed strongly and due to the moisture a wide band is appeared⁽¹⁴⁾.

Figure 5, shows the IR spectrum of the bridged complex of PzFe with DCN. It shows a band at 2250 cm^{-1} which could be attributed to the $\text{C}\equiv\text{C}$ of the cyanide of DCB bridge^(15, 16)

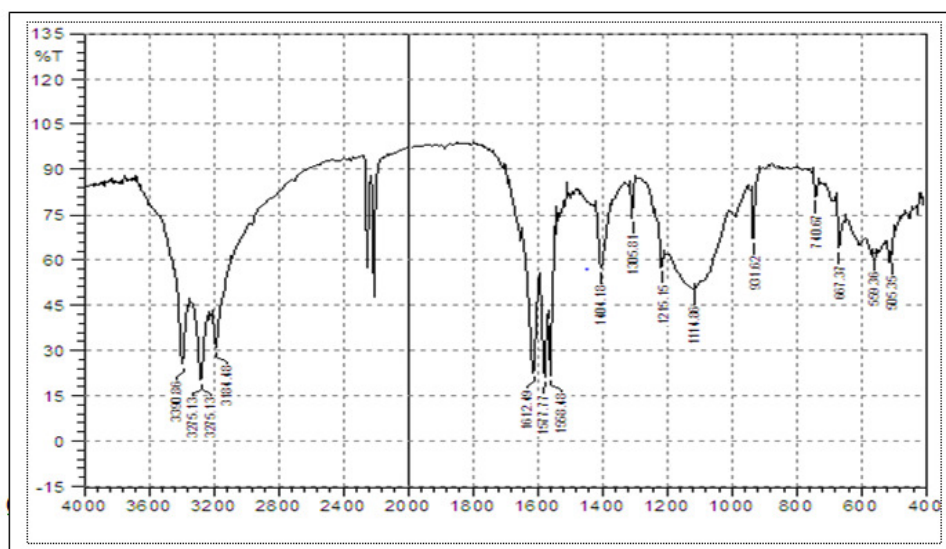


Figure 4: IR spectrum of the complex, PzNi

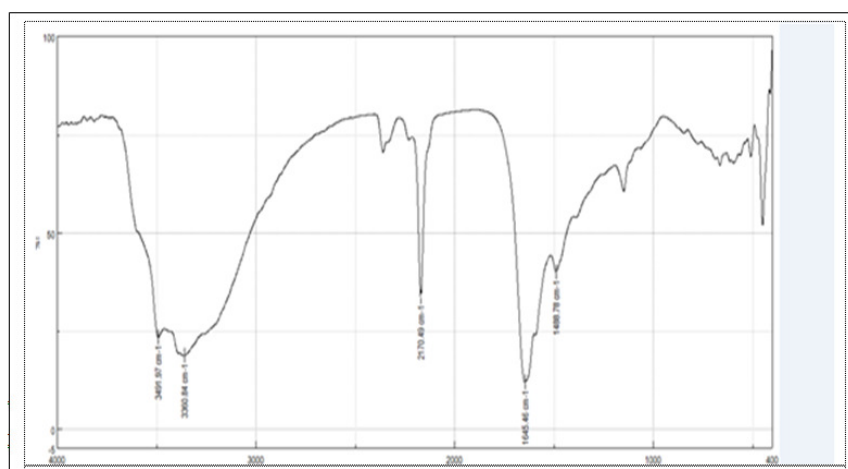


Figure 5: IR spectrum of $(\text{PzNiDCB})_n$

Figure 5: IR Spectrum of the Complex $(\text{PzNi}(\text{DCN}))_n$

¹H-NMR: Figures 6 shows the ¹H-NMR spectra of the complex PzNi bridged with DCB in DMSO. It shows unresolved chemical shift at 5.3 ppm while it doesn't show the aromatic and other features which refers that the central metal is paramagnetic and might interact with other protons which makes the signals appear in far low field⁽¹⁷⁾ and the nitrogen of DCB ligand didn't make electron pairing to the two single electrons of the metal. The elemental analysis and IR shows the formation of (PzNi(DCN))_n. Which might refers to the formation of triangular bipyramidal (dsp³ or sp³d hybridization) or octahedral with DCN bridging (sp³d² hybridization). Leaving the free electrons unpaired.

The protons of the DMSO and the moisture shows shifts at 3.75 and 2.48 ppm respectively⁽¹⁵⁾.

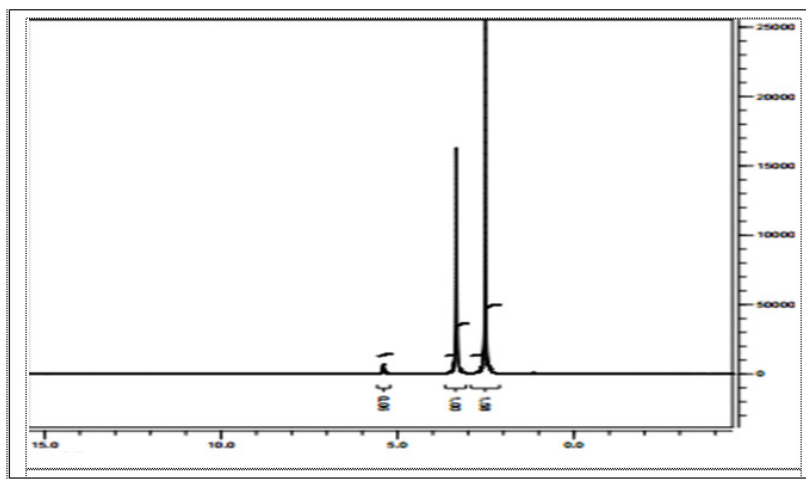


Figure 6: The ¹H-NMR Spectrum of the Complex PzNi(DCB)

The Electronic Spectra: Figure 7 shows the electronic spectra of the complex PzNi bridged with with the DCB.

It shows the characteristic bands of phthalocyanine and tetrapyrazinoporphrazines^(16,18). Q-band at 670 nm ($\epsilon = 0.51 \times 10^5$ l.mol⁻¹cm⁻¹) and Soret band at 390nm ($\epsilon = 1.1 \times 10^5$ l.mol⁻¹cm⁻¹).

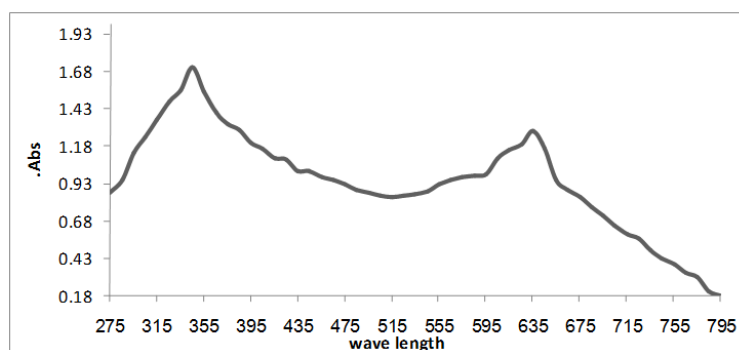


Figure 7: The Electronic Spectrum of the Complex Bridged with DCB

Thermogravimetric Analysis

The thermogram in figure 8 shows two steps of the weight loss of the bridged complex, (PzNi(DCN))_n: 1- At (50_140)⁰C with two Tmax at 96.88⁰C and 132.72⁰C with percent loss 2.7% (calculated 2.7%) which refers to the loss of water molecule^(19,20). 2- At 150-290⁰C with Tmax at 230.01⁰C and percent loss of 5.3%(calculate 5.2%) which might refers

to the loss of four ammonia molecules.3- At 300-590⁰C with Tmax of two steps 425.60⁰C and 511.62⁰C and percent loss of 14.61%(calculate 14.3%) which might refers to the loss of 1-4 dicyanobenzene and ethylenediamine molecules.

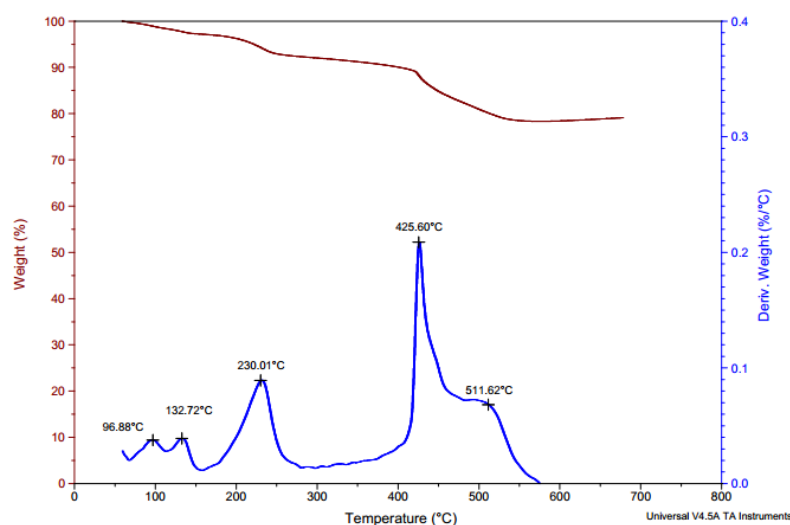


Figure 8: Thermogram of (PzNi(DCB))_n

X-ray Diffraction Analysis: Figures 9 shows the X-ray diffraction of (PzNi(DCN))_n using CuK_α (1.5406Å) as X-ray energy source and using powder method. The most important estimated d-spacing is 4.21Å (⁰2θ=21.08) with relative intensity 100% and d-spacing 3.59Å (⁰2θ=24.79) with relative intensity 56.14%. The main d-spacing of 100% intensity shows that the compound have bigger d-spacing than the unbridged stacked structures⁽²¹⁾.

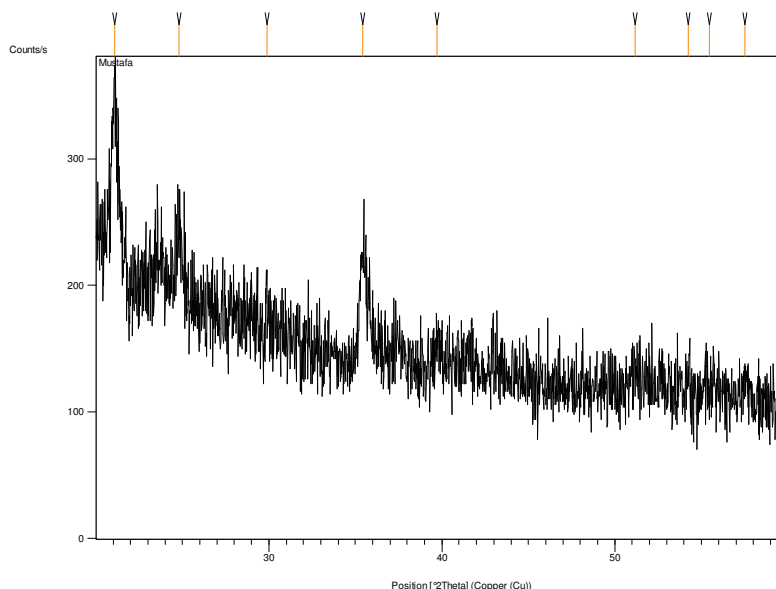


Figure 9: The X- Ray Diffraction of (PzNi(DCB))_n

Electrical Properties

The dc electrical properties were measured using system containing cryostat, power supply, voltmeter, ammeter and temperature measurement system. The cryostat contains tube in which the sample is inserted and connected to a conducting wires. The tube can be evacuated and heated. The temperature is measured by thermocouple. The sample is

surface film casted on a glass substrate. The conductivity was measured under vacuum of 10^{-4} tor. Figure 10 shows the V-I characteristic curves at different temperatures. It shows a clear ohmic relation in the first 10 volts.

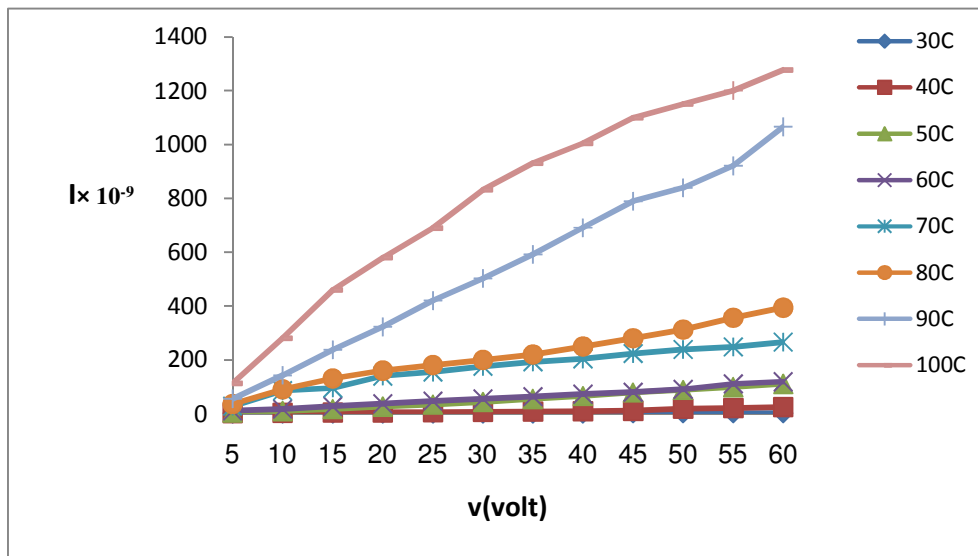


Figure 10: The V-I Characteristic Curve for $(\text{PznNi}(\text{DCB}))_n$ (I Current, μA)

Figure 11 shows the relation between the dc conductivity ($\ln \sigma$) and the inverse temperature, at 10 Volts, according to Arrhenius equation ($\ln \sigma = \ln \sigma_0 - \frac{\Delta E}{kT}$) where σ_0 , ΔE , k and T are the pre-exponential factor, activation energy, Boltzmann constant and absolute temperature respectively⁽²²⁾. The activation energy between valence and conduction bands was estimated from the slope to be 1.12 eV compared to the activation energy estimated for PzFe which is equal to 0.9 eV⁽²³⁾. The higher activation energy of the bridged complex might be due to the wider separation between the $(\text{PzFe}(\text{DCN}))_n$ planes in compared to the stacked structure of the PzFe ⁽⁹⁾.

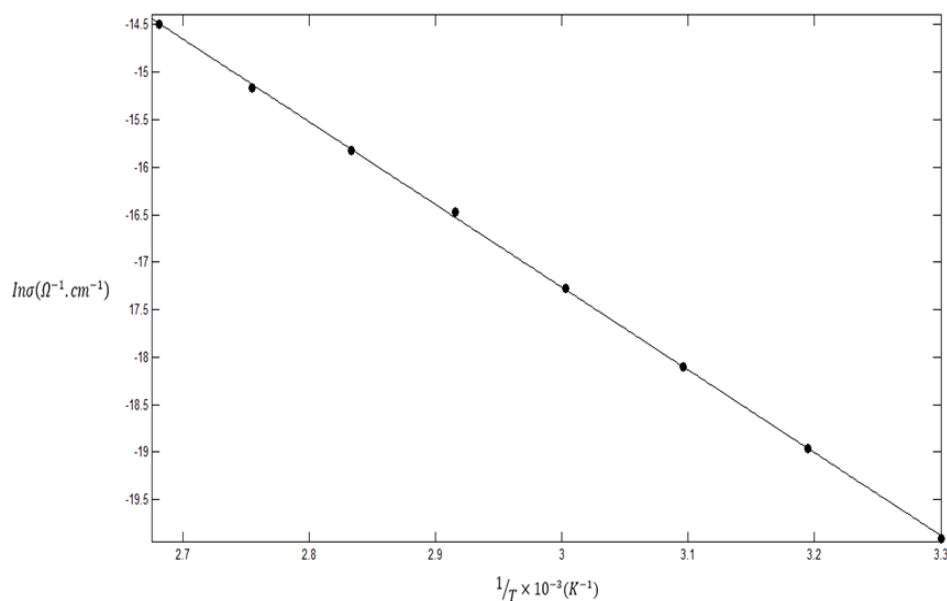


Figure 11: The Relation between and Inverse Temperature for the Complex $(\text{PzFeDCB})_n$

CONCLUSIONS

From the study we can conclude that the prepared complex is of the bridged structure $(PzFeDCB)_n$ and behaves as semiconductor.

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